Structure evaluation of an alloy single crystal surface, Au₃Pd (113), by low energy ion scattering

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Abstract

Low energy ion scattering in the NICISS (neutral impact collision ion scattering spectrometry) mode and surface channeling are used to study the surface structure of a single crystal alloy, Au₃Pd. The crystal belongs to the fcc class. At the surface Au segregation is found. The surface is not bulk terminated. The top rows of the surface are the $[1\bar{1}0]$ rows which are formed by Au atoms. Pd atoms are found in the second layer only. © 1998 Elsevier Science B.V.

1. Introduction

Low energy ion scattering has been used for surface structure analysis to some extent [1]. The studies include the surfaces of single crystal alloys. More recently Cu_3Au (100) and (110) [2], Au_3Cu (001) [3], Cu_3Pt (111) [4], Ni_3Al (100) and (110) [5] and Cu_3Au (100) [6] have been analyzed by ion scattering methods. In these studies other methods, e.g. LEED, STM, are used too. As a general conclusion from the work quoted here we find a strong tendency for surface segregation. Especially in the case of the Au-containing alloys Au tends to segregate to the surface [2,3]. The surface of the Cu rich Cu_3Au is bulk terminated with a rippling effect, i.e. the Au atomic rows are displaced relative to the Cu rows of the surface [6].

In the present work we study the Au_3Pd (113) surface using different modes of low energy ion scattering and LEED.

2. Experiment

The experimental setup is a UHV system with an ion source operating between 200 V and 15 kV, a sector field magnet for the ion beam analysis, beam forming lenses and diaphragms, a target manipulator, a LEED system, a time-of-flight (TOF) system and an electrostatic analyser for low energy ion scattering spectroscopy (LEIS). The TOF-system uses a beam pulser and channelplate detector set at a scattering angle of 165°. Further details of the experiment are described elsewhere [7,8]. Since this is the first study of Au_3Pd the target preparation was time consuming in order to reach reproducible surface conditions. It took several weeks of sputtering and annealing cycles before satisfactory LEED results were obtained. Target

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cleanliness was obtained after a few days only. In agreement with the LEED data also the azimuthal scans using the TOF-system in the surface blocking mode did not show satisfactory results in earlier stages of the surface preparation. The surface blocking is one of the three ion beam methods we used in the experiment. In the surface blocking mode the beam energy and the (grazing) angle of incidence are kept constant and the azimuthal angle is varied. At small angles of incidence, approximately 10°, and a large scattering angle, here 165°, the azimuthal scans show yield minima at the low index surface directions. For fcc (110) surfaces the most pronounced minima are obtained for the [1$\bar{1}$0], [1$\bar{1}$1], [1$\bar{1}$2] and the [001] directions [1]. The second ion beam method applied is NICISS (neutral impact collision ion scattering spectrometry) which affords a quantitative analysis of surface lattice constants [1]. In this ion beam method the beam energy and the azimuthal angle are fixed and the angle of incidence is varied. The third method is LEIS as mentioned earlier.

3. Results and discussion

The first results are LEIS spectra of the clean Au_3Pd surface. The surface is cleaned by sputtering followed by annealing up to 870 K. The LEED pattern connected with the clean surface is (1×1)

indicating no irregularities. The ion spectra using Ne^+ (Fig. 1) and He^+ ions show no impurities. The Ne spectra show a larger Au/Pd ratio than expected from the bulk concentration of 3:1. During the preparation a preferential sputtering of Au is observed. The annealing is connected with a Au segregation obviously. Other Au rich crystals show comparable sputtering and segregation effects [3,4]. At lower grazing angles of incidence and at an azimuthal angle off the [1$\bar{1}$0] surface direction the Pd signal decreases due to the blocking by the Au top layer atoms.

The azimuthal scan (Fig. 2) for the Ne–Au signal shows the minimum for the [1$\bar{1}$0] direction and a minimum for the [$\bar{1}$20] direction, 73.22° off the [1$\bar{1}$0] direction. The main structure is, besides the [1$\bar{1}$0] minimum, a broad valley including the [1$\bar{4}$1] direction 33.56° off the [1$\bar{1}$0] direction and the [0$\bar{3}$1] at 47.87° off [1$\bar{1}$0]. This observation is the signature a (113)-surface in agreement with LEED pattern. Fig. 3 shows the two possible bulk terminated structures of Au_3Pd (113).

The NICISS results are used here for a more detailed analysis of the surface composition of the Au_3Pd (113) surface. For each surface direction we observe two peaks in the experimental spectra. In the NICISS experiment each ion scatters from two surface atoms. The first atom deflects the ion by a small scattering angle, thereby forming a 'shadow cone' [1]. The second atom is hit under a small impact parameter hence the ions are scat-
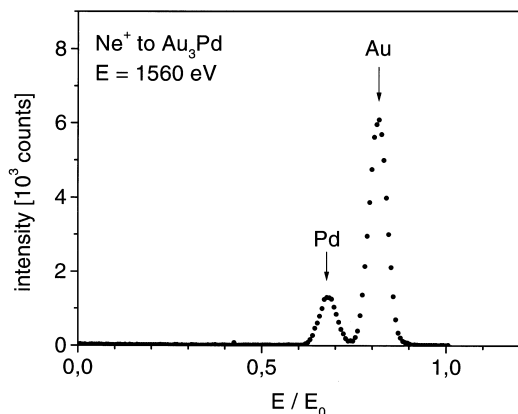

Fig. 1. Ne ion backsattering spectrum from Au_3Pd (113). The primary energy is 1560 eV, the angle of incidence 45° and the scattering angle is 90°.
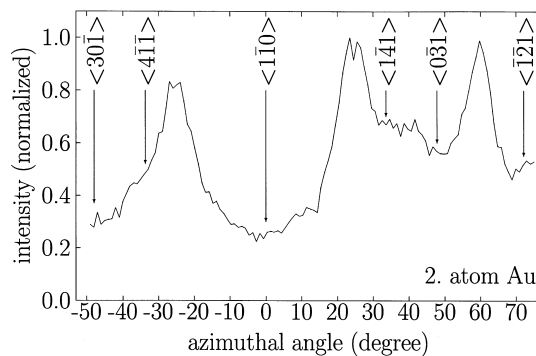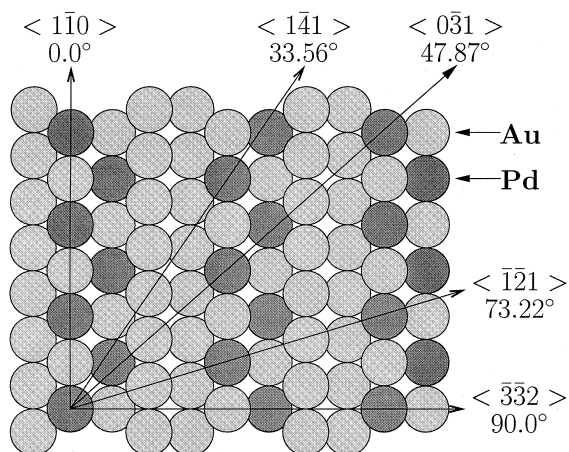

Fig. 2. Azimuthal scan with Ne ions of the Au_3Pd (113) surface for the Au peak. Ne ions at a primary energy of 2080 eV are used. The angle of incidence is 11.5°, the scattering angle is 165°.

Fig. 3. Bulk terminated model of the Au_3Pd (113) surface.

tered by a large angle. The scattering from the second atom, Au or Pd, causes the elastic energy loss such that two peaks can be separated in the TOF spectra. Fig. 4 shows the variation of the ion yield the 'Au-peak' with increasing angle of incidence. The experimental data are compared with calculations based on a two-atom scattering model [1]. The calculation uses a Ziegler–Biersack–Littmark-potential and surface thermal vibrations according to the Debye-model. Surface Debye-temperatures of $\Theta_{Pd} = 73$ K and $\Theta_{Au} = 80$ K are used. In Fig. 4(a) the calculation is for a pure Au-[1$\bar{1}$0] surface chain and in Fig. 4(b) for a mixed Pd–Au chains. The agreement for the Au–Au chains is better than for the 1:1 Pd–Au chains.
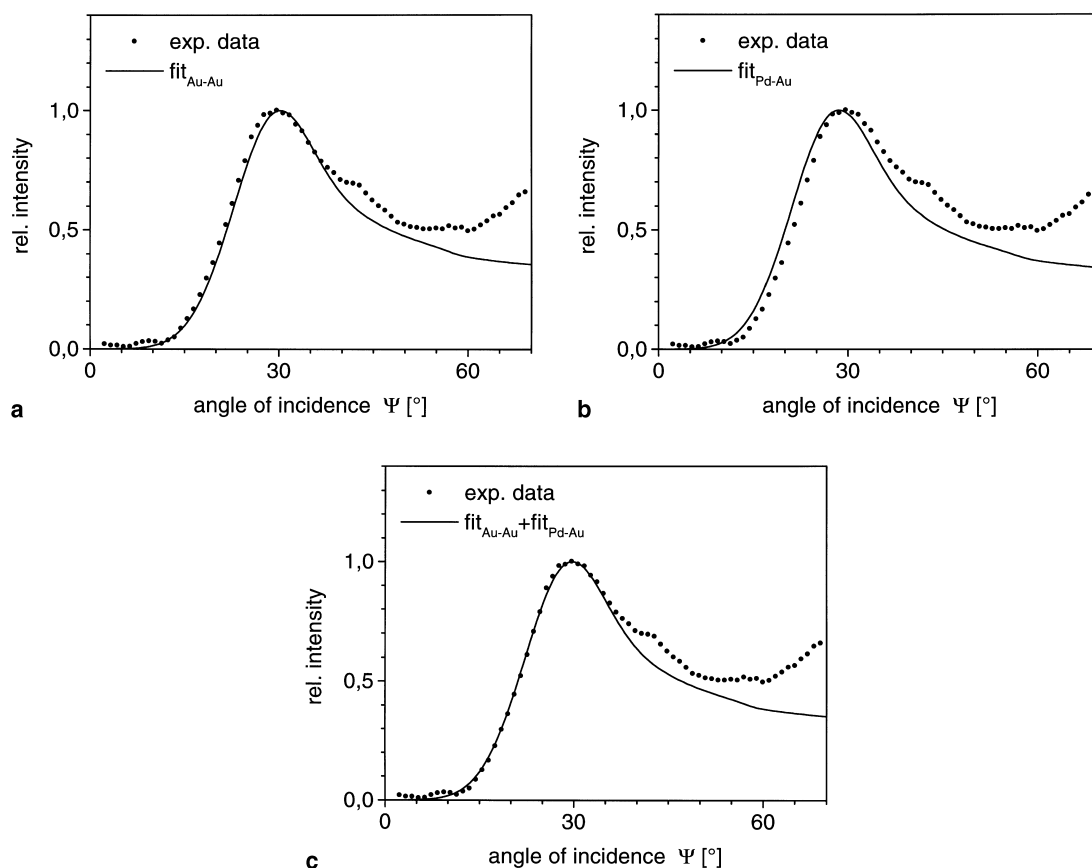

Fig. 4. (a) NICISS data for the Au peak using Ne^+ at 2080 eV and a scattering angle of 165° for the [1$\bar{1}$0] surface chains. The solid line is calculated for pure Au chains. Mean square deviation 3%. (b) Experimental data as in (a). The calculation is for mixed Pd–Au chains. The first atom forming the shadow cone is Pd, the large angle backscattering occurs of Au. Mean square deviation 6.9%. (c) Experimental data as in (a) The calculation is a sum of pure Au atom pairs and Pd–Au pairs at a ratio 4:1. Mean square deviation 0.3%.

The agreement is improved when a mixture of Au–Au and Pd–Au atom pairs is assumed. A ratio of four Au–Au pairs per Pd–Au pair gives the best result (Fig. 4(c)). The root mean square deviations between experiment and calculation decrease from 3.0% (Fig. 4(a)) and 6.9% (Fig. 4(b)) to 0.3% (Fig. 4(c)). This result allows the conclusion, that the second layer [1$\bar{1}$0] chains are mixed Au–Pd chains with an approximate concentration of 2.5:1 since we know that the top layer contains Au only. The fit includes the result, that the atomic distance in Au–Au [1$\bar{1}$0] chains is with 2.81 ± 0.05 Å marginally shorter than expected for the alloy with a [1$\bar{1}$0] = 2.85 Å.

The corresponding results for the Pd peak of the NICISS spectra are shown in Fig. 5. For the calculations the same model is used. The root mean square deviations are for the Pd–Pd case 3.5% (Fig. 5(a)) and for the Au–Pd case 5.8% (Fig. 5(b)). The best agreement with an error of 2.2% is obtained for a mixed system with a ratio of Au–Pd to Pd–Pd pairs of 2.5:1. This result is compatible with pure Au–Au top layer [1$\bar{1}$0] chains and mixed second layer chains. The presence of Pd–Pd pairs is, however, evidence for disorder in the second layer, i.e. the second layer chains are not Au–Pd–Au... chains as may be concluded from the Au–NICISS data. The NICISS
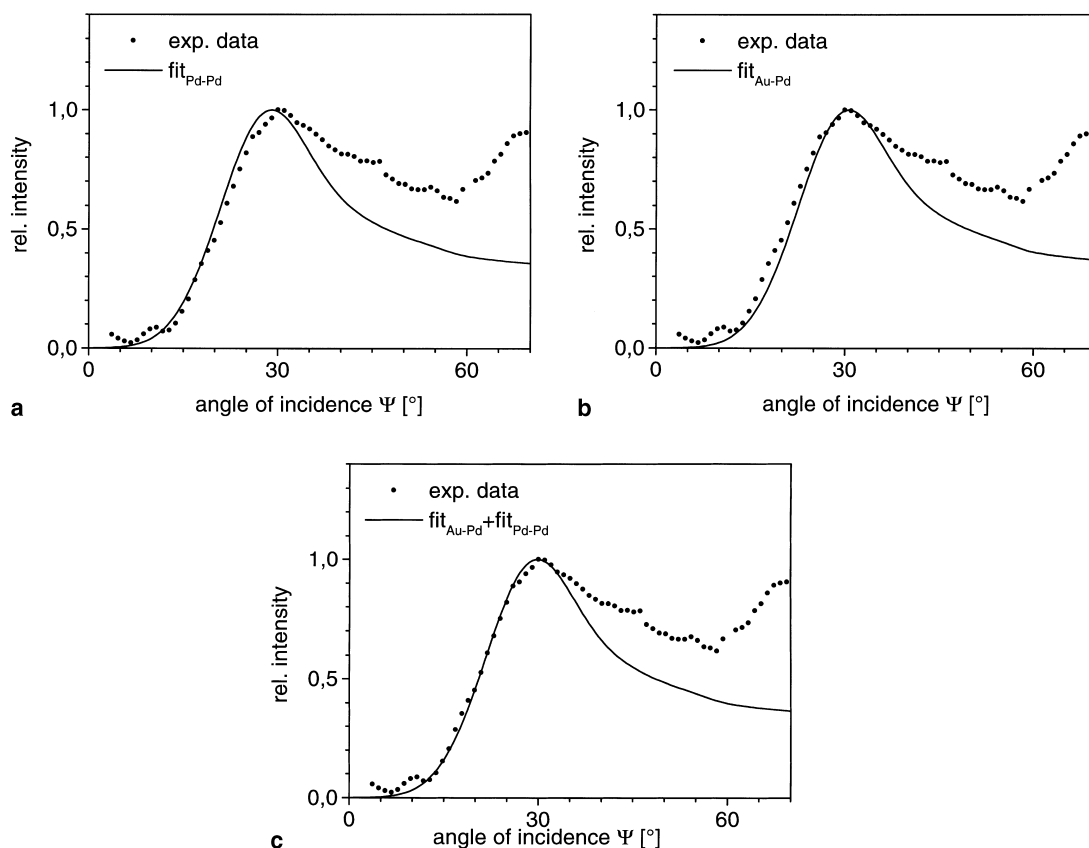

Fig. 5. (a) NICISS data for the Pd under the experimental conditions of Fig. 4. The solid line is calculated of pure Pd chains. Mean square deviations 3.5%. (b) Experimental data as in (a) The calculation is for Au–Pd chains. Mean square deviation 5.8%. (c) Experimental data as in (a) The calculation is the sum of Au–Pd and Pd-Pd atom pair scattering at a ratio of 2.5:1. Mean square deviation 0.3%.

analysis of other surface directions will be published elsewhere [9].

4. Summary

Ion scattering methods were applied to determine the structure and composition of a Au_3Pd (113) surface. The Au_3Pd (113) surface shows Au segregation such that the top $[1\bar{1}0]$ atomic rows contain Au only. The second layer rows are mixed, disordered Au–Pd rows.

Acknowledgements

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